In Situ Oxidation

Results from Multiple DoD Sites

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Technology Status: In Situ Oxidation

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- Marvin Unger/RETEC
- Joe Gormley/RETEC
- Ray Arguello/Blue Chip Engineering

www.estcp.org/technical_documents

Background

- Rapid Adoption of ISO for NAPL Sites
- Low-Cost, Rapid Source Destruction
- C=C and C–C Bonds Attacked
- H_2O_2, $KMnO_4$, and O_3 Used
- Mixed Results From Applications

Chemistry

- $3H_2O_2 + C_2HCl_3 \longrightarrow 2CO_2 + 2H_2O + H^+ + Cl^-$
  - $Fe^{2+} + H_2O_2 \longrightarrow Fe^{3+} + OH\cdot + OH^-$
  - $Fe^{2+} + OH\cdot \longrightarrow Fe^{3+} + OH^-$ (Acidic)

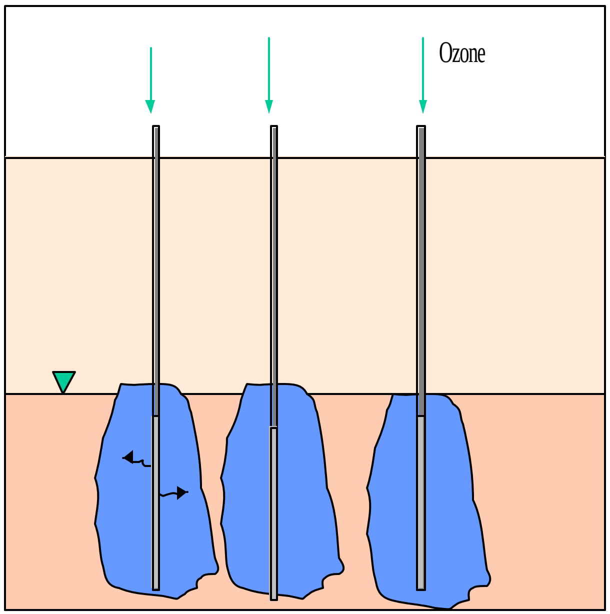
- $2MnO_4^- + C_2HCl_3 \longrightarrow 2CO_2 + 2MnO_2 + 3Cl^- + H^+$
  - MnO_4^- (Liquid) $\longrightarrow$ MnO_2 (solid)

Engineering Issues

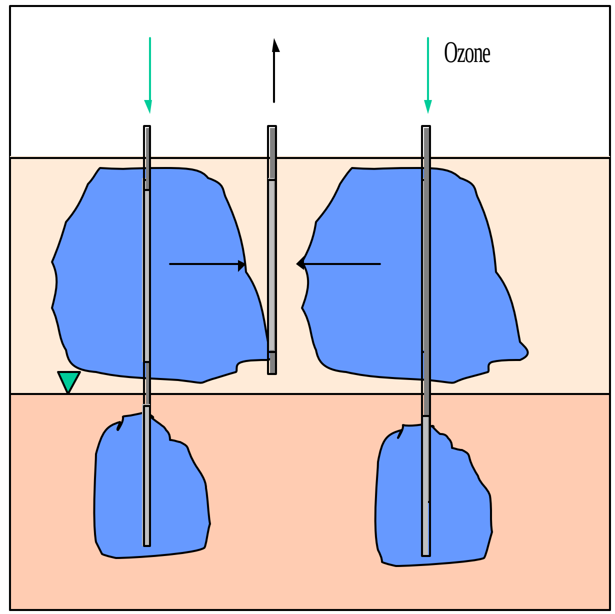
- Delivery Systems
- Mixing Enhancements
- Efficiency of Oxidant Use
- Targeting Source Areas

Delivery Methods

Liquid Oxidant Injection

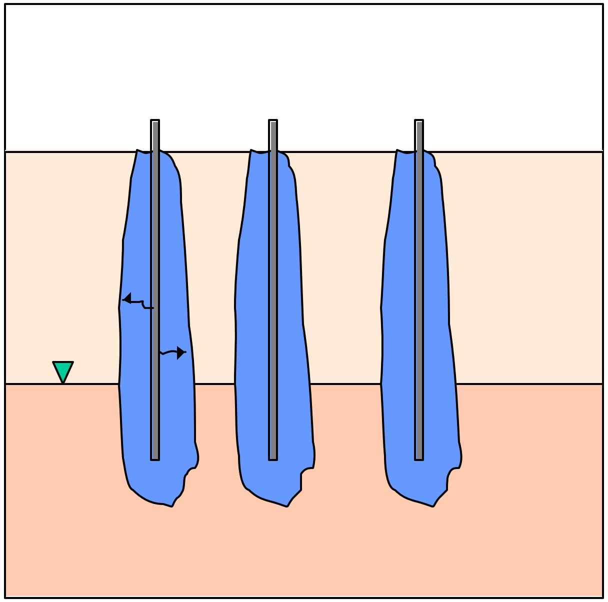


Gaseous Oxidant Injection

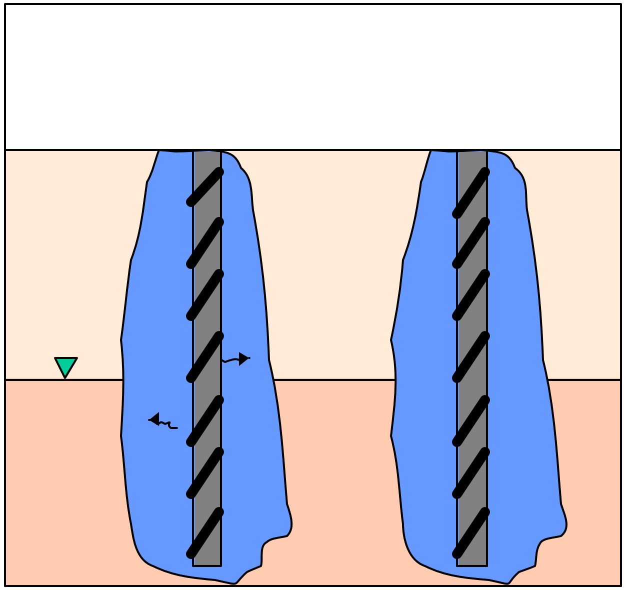


Delivery Methods

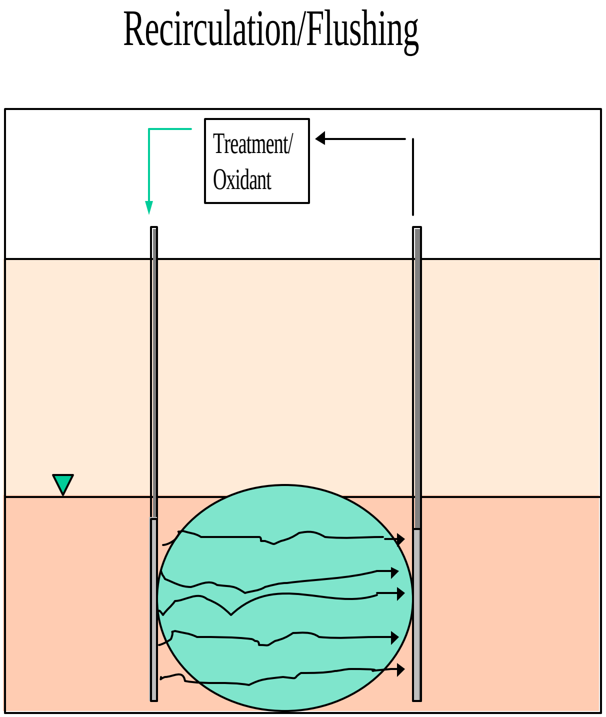
Lance Permeation

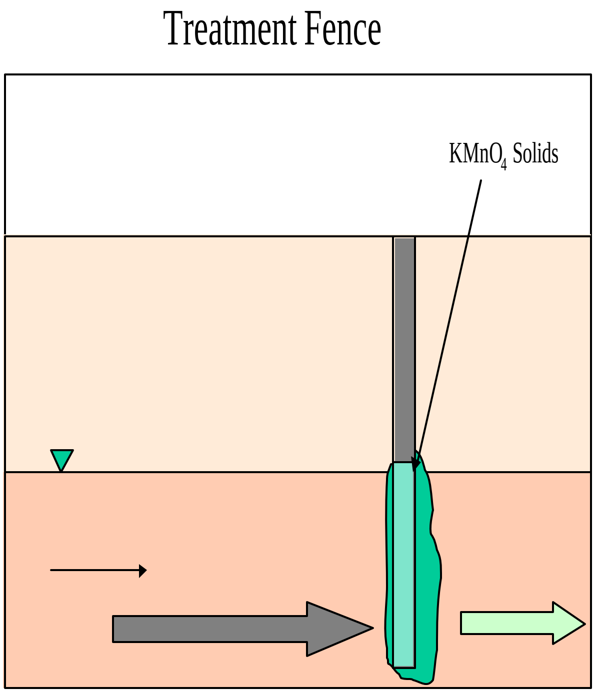


Deep Soil Mixing



Delivery Methods





Arthur Canon Doyle

The Adventure of the Copper Beeches

1892

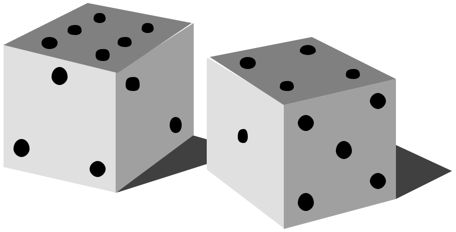
“What is the meaning of it all, Mr. Holmes?”

“Ah. I have no data. I cannot tell”, he said.

Oxidants: Key Features

Influencing Factors	H_2O_2	$KMnO_4$	O_3
pH	Prefer pH 2-4, feasible to near neutral.	Prefer pH 7-8, effective over wide range.	Effective at natural soil pH.
NOM/Reduced Species	Any reduced species exert a demand for oxidant, especially natural organic matter (NOM) and reduced inorganics.		
Oxidant Degradation	Easily degraded on contact with soil/groundwater.	Oxidant is very stable.	Ozone degradation in soil is limited.

Technology Concerns



- Explosion Prevention
- Insufficient Mixing and Contact
- Rebound in Groundwater Concentrations
- Recalcitrance of Some VOCs
- Potential for Volatile Emissions of VOCs
- Plugging and Short-Circuiting
- Little Design and Operating Guidance

Objectives

- Establish Selection and Design Basis
- Determine Cost and Performance
- Evaluate Reasons for Success or Failure
- Provide Initial Guidance For ISO Use

Approach

- Phase 1: Survey Sites
  - Treatment Approach
  - Ability to Meet Objectives

- Phase 2: Site Profiles
  - Site Characteristics
  - Design Basis and Rationale
  - Cost and Performance
  - Technical Concerns/Problems

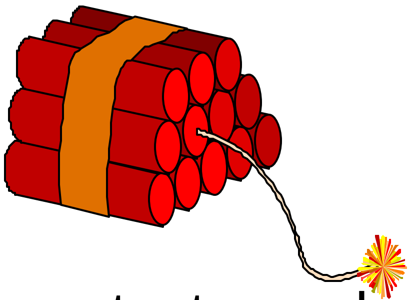
Cost Factors

- Depth and Thickness
- Contaminant Type and Mass
- Other Oxidizable Compounds
- Well Spacing
- Mixing Enhancements
- Number of Injections
- Need for pH Adjustment

Performance Summaries: Unsaturated Soils

Site	Loss	Concerns
1	90%	Several areas > soil cleanup levels
2	70%	Injection screen placement not optimal Spatial variability complicated analysis
3	67%	VOC off-gassing during deep soil mixing Low permeability soils limited $KMnO_4$ penetration into soils
4	77%	VOC off-gassing

Performance Summaries: Saturated Soils



Site	Loss	Concerns
5	-	Explosion terminated project
6	97%	Rebound observed; Active treatment stopped
7	99%	New hot spots discovered
9	?	Rebound; Equipment failure
10	95%	Rebound; Short-circuiting
11	<5 ppb	Some dead zones with DNAPL remained
12	94%	Rebound; VOC stripping; Remnant DNAPL
13	50%	Rebound; VOC stripping; High oxidant demand

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Cost Estimates

Site	Cost/lbVOC	Scale
4	$190	Full
6	$375	Full
12	$900	Pilot
13	$8,700	Pilot

Potential Detrimental Effects

- Particulates can be generated and permeability loss is possible.
- Gas evolution with peroxide and ozone.
- Generation of fugitive emissions.
- Potentially toxic byproducts.
- Reduction of biomass.

Lessons Learned

- Site Characterization
  - Total Oxidant Demand
  - Contaminant Delineation
  - Mass Estimates
  - Vapor Monitoring

Lessons Learned

- Design Issues
  - Radius of Influence
  - Oxidant Concentration
  - Enhance Mixing

Lessons Learned

- Operational Issues
  - Multiple Injections
  - Vapor Monitoring
  - Monitor for Rebound

Research & Implementation Needs

- Better DNAPL Site Characterization
  - Stratigraphic Information and DNAPL Detection
- Better Definitions of Success
  - Goals and Measurement Parameters
- Better Design Basis and Models
  - Radius of Influence/Oxidant Efficiency/Mixing
- Better Transport and Mixing
- Better Understanding of Loss Mechanisms
  - Oxidation/Dilution/Volatilization

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Case Study: Irvine, CA

- Chlorinated solvents (PCE, TCE) in perched ground water (12-16 feet bgs)
- Silty Materials (10^{-5} cm/sec)
- Active remediation (vapor extraction + pump and treat)
- Total Fluids Extraction Proposed
- “Well-Characterized” Source and Plume

In Situ Oxidation Goals

- Stop Active Remediation
- Achieve Closure/Natural Attenuation
- Prevent Total Fluids Extraction
- Remove Source to Extent Practicable

Approach

- 4 Injections of 5% $KMnO_4$ at 2-Month Intervals: Injection Wells and Geoprobe
- Adjust Locations Based on Monitoring
- Injected 2500 Lbs Total for Estimated 50 Lb CVOCs
- Pressure = 100-150 psig; Rate = 2 gpm
- ROI = 10’ (design), 25-30’ (actual)

Findings

- Source Larger and More Complex than Investigation Indicated
  - Higher concentrations
  - New contaminants (MC, Not oxidized)
- Permanganate Lasted 2-4 Months
  - Rebounds after every injection
- Significant Plugging After First Injections
- Project Goals Achieved
- Cost << Total Fluids Extraction
  - $80/cu. yd / $375/lb CVOC treated